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Citation: Appl. Phys. Lett. **80**, 1114 (2002); doi: 10.1063/1.1448387
View online: http://dx.doi.org/10.1063/1.1448387
View Table of Contents: http://aip.scitation.org/toc/apl/80/7
Published by the American Institute of Physics

Two-photon absorption properties of commercial fused silica and germanosilicate glass at 264 nm

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(Received 3 October 2001; accepted for publication 3 December 2001)

Using high-intensity femtosecond pulses at $\lambda = 264$ nm, we have measured the two-photon absorption (TPA) coefficient in three fused silica samples Suprasil, Herasil, Infrasil (Heraeus) and in 3.5 mol % Ge-doped fused silica. While in fused silica samples the TPA coefficient value is about 2×10^{-11} cm/W, in germanosilicate glass it equals $(42\pm3)\times10^{-11}$ cm/W. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1448387]

Over the last decade ultraviolet (UV)-induced refractive index change in germanosilicate glass was widely used for the production of fiber Bragg gratings.[1] The gratings could be inscribed by both low-intensity and high-intensity UV light through one-quantum and two-photon mechanisms, respectively.[2–4] It was shown[1] that very large and thermally stable refractive index modulations are formed in Ge-doped fused silica by high-intensity (10^8 W/cm^2) UV light provided by KrF*($\lambda = 248$ nm) and ArF*($\lambda = 193$ nm) excimer lasers. Similarly, the high-intensity UV laser excitation of pure fused silica also produces refractive index changes by two-photon excitation.[5,6]

There is no evident correlation between the doping concentration in germanosilicate glass and linear absorption properties in 5.1 eV (241 nm) energy band. The intensity of this band is determined by the concentration of oxygen deficient centers, and depends mostly on the conditions of glass or fiber fabrication. Knowledge of the two-photon absorption (TPA) coefficient could be important for optimal choice of material used for Bragg grating inscription.

In our previous work[7] we have measured the TPA coefficient for fused silica and crystalline quartz with 10% accuracy. Here we report the determination of TPA coefficient for germanosilicate glass in comparison with three commercial fused silica samples.

The fused silica samples (disks Φ 2.54 cm$\times$1 cm or Φ 2.54 cm$\times$0.1 cm) were supplied by Heraeus. We used three types of fused silica glass: Suprasil, Herasil, and Infrasil with OH content $\leqslant$1000, $\approx$150 and $\leqslant$8 ppm, respectively. The linear absorption coefficient α at 264 nm, measured by a HP 8453 spectrophotometer (Agilent Technologies), was equal to $\leqslant$0.001, 0.02, and 0.02 cm^{-1} for Suprasil, Herasil, and Infrasil, respectively. The Ge-doped fused silica sample was cut from vapor phase axial deposition (VAD) fiber preform in the form of a rectangular plate 0.8 cm$\times$3.4 cm with thickness 0.085 cm. The molar concentration of GeO_2 in our sample measured by energy dispersive x-ray analysis was 3.5 mol %. The linear absorption coefficient was 2.8 cm^{-1} at 264 nm and 46.6 cm^{-1} at 241 nm.

To measure the TPA coefficient we used the transmittance approach.[7] The fourth harmonic radiation ($\lambda = 264$ nm, $\tau = 220$ fs, $\Delta f = 27$ Hz) of Nd:glass laser (Twinkle, Light Conversion Ltd., Vilnius, Lithuania) was directed into the sample. A long focal length (454 mm) fused silica lens was used to change the laser beam cross-sectional area and hence the incident intensity, which was varied in the range 5–30 GW/cm^2. The sample position was well in front of the lens focal point in order to prevent self-focusing (see Ref. 7 for details).

The Twinkle laser system generates UV laser pulses with Gaussian shape in time and in space.[8] We can choose the following representation for Gaussian beam:

$$I_{\mathrm{inc}}(r,t) = I_0 \exp\left[-2\left(\frac{r}{w_0}\right)^2\right]\exp\left[-\left(\frac{2t}{\tau_p}\right)^2\right], \tag{1}$$

where I_0 is the maximum on-axis intensity, τ_p is the pulse width at the e^{-1} level, and $w_0/\sqrt{2}$ is the beam radius at e^{-1} level [at full width half maximum (FWHM) $\tau = \tau_p\sqrt{\ln 2}$, $w = w_0\sqrt{2\ln 2}$]. After integration over space and time, the pulse energy ε_0 is given by

$$\varepsilon_0 = \int_{-\infty}^{+\infty} dt \int_0^{+\infty} I_{\mathrm{inc}}(r,t)\,2\pi r\,dr = \frac{\pi\sqrt{\pi}}{4} I_0 \tau_p w_0^2. \tag{2}$$

To find the transmitted energy $\varepsilon_{\mathrm{tr}}$, we integrate the transmitted intensity over space and time, using the well-known formula for the transmitted intensity through the medium in the presence of linear and nonlinear (two-photon) absorptions (see, for example, Ref. 9). The energy transmittance is then given by the expression:

$$T = \frac{\varepsilon_{\mathrm{tr}}}{\varepsilon_0} = \frac{\alpha T_0}{\sqrt{\pi}\beta I_0 (1-R)[1-\exp(-\alpha l)]} \times \int_{-\infty}^{+\infty} \ln\left\{1 + \frac{\beta}{\alpha} I_0 (1-R)[(1-\exp(-\alpha l)] \times [\exp(-k^2)]\right\} dk, \tag{3}$$

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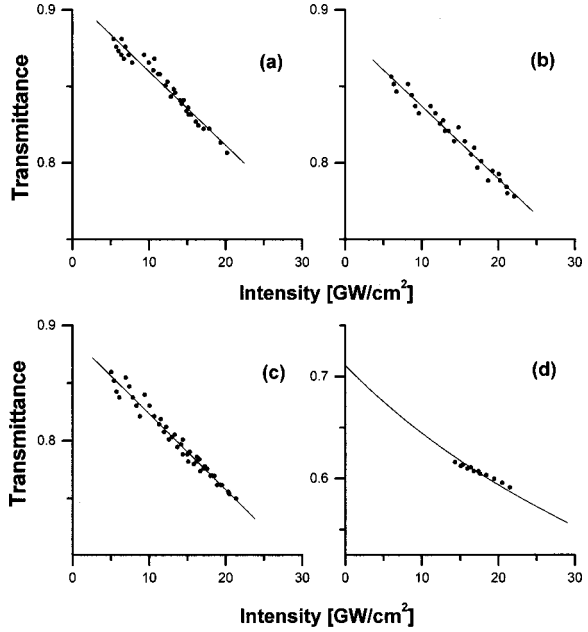

FIG. 1. The typical curves of the transmittance-irradiance dependence measured at 264 nm for Suprasil (a), Herasil (b), Infrasil (c), and Ge-doped fused silica (d). The fitting gave the following values for the TPA coefficient (in 10^{-11} cm/W): (a) 1.58, (b) 1.61, (c) 1.87, and (d) 42.8.

where α is the linear absorption coefficient, β is the two-photon absorption coefficient, l is the length of the medium, R is the reflectivity of the sample at normal incidence, $T_0 = (1-R)^2 \exp(-\alpha l)$ is the transmittance at zero-intensity limit, and $k = 2t/\tau_p$.

The energy transmittance at low intensities (and/or at low β values) can be approximated by a linear function of irradiance I_0 (linear approximation):

$$T_{I_0 \to 0} = \frac{\varepsilon_{\mathrm{tr}}}{\varepsilon_0} = T_0 \left[1 - \frac{\beta I_0 (1-R)[1-\exp(-\alpha l)]}{2\sqrt{2}\alpha} \right]. \quad (4)$$

Measuring the slope of this dependence gives the two-photon absorption coefficient.

In order to account for the change of maximum on-axis intensity due to focusing and focus distance prolongation in the sample, we replace I_0 in Eqs. (3) and (4) by the corrected value.[7]

It is well known that accurate determination of the TPA coefficient requires the precise knowledge of beam diameter and pulse-width. The former was found by placing an aperture symmetrically to the axis of the beam and measuring the energy trasmittance through it (see, for example, Ref. 10). Such a procedure is valid as we have preliminary information that our laser pulse has Gaussian shape in space.[8] The weighted average value for the laser beam radius was 2.56 ± 0.03 mm (3.01 ± 0.04 mm FWHM).

For UV laser pulse width measurement we employed the TPA-based autocorrelation approach.[11,12] . The mean value of pulse duration for a series of four measurements was found to be $\tau = 220 \pm 10$ fs (FWHM).

We have measured the transmittance of six 1 cm samples of fused silica, two of each type, and one 0.085 cm sample of germanosilicate glass as a function of input laser beam irradiance. Figure 1 represents typical experimental dependencies for Suprasil (a), Herasil (b), and Infrasil (c). It is seen from Fig. 1, that the recorded dependencies (a), (b), and (c) allow linear fitting according to Eq. (4). Table I contains the experimental data for β values obtained in every series of experiments and the averaged data for each glass. The absolute uncertainty of β (6%) is predominantly due to the uncertainty of the irradiance, which consists of the errors in the energy calibration (3%), the pulse duration reproducibility (4.4%), and the determination of the laser beam's cross-sectional area (2.3%). Therefore, the total uncertainty of β determination in our experiments was about 10%.

TABLE I. Experimental data on β values for fused silica glasses and Ge-doped fused silica (in 10^{-11} cm/W)

Glass	Overall β values[a]	Averaged β value
Suprasil	1.92	1.7 ± 0.2
	1.61	
	1.58	
	1.31	
	1.58	
	2.09	
	1.95	
	1.17	
Herasil	1.64	1.8 ± 0.2
	1.77	
	2.03	
	1.61	
	1.49	
	1.59	
	1.81	
	2.00	
	1.90	
Infrasil	2.22	2.1 ± 0.2
	2.17	
	1.60	
	2.03	
	2.37	
	2.22	
	1.87	
	2.29	
3.5 mol % Ge-doped fused silica	44.7	42 ± 3
	44.6	
	44.8	
	42.8	

[a]Absolute error (6%) was added to the averaged β values.

In Table I Suprasil has the smallest β value $(1.7 \pm 0.2) \times 10^{-11}$ cm/W, Herasil has a larger β value $(1.8 \pm 0.2) \times 10^{-11}$ cm/W, and Infrasil the largest one, $(2.1 \pm 0.2) \times 10^{-11}$ cm/W. The measured value for Suprasil from Heraeus coincides well with our data for other Suprasil glasses, $\beta = (1.9 \pm 0.2) \times 10^{-11}$ cm/W for Corning 7940 and $\beta = (1.9 \pm 0.1) \times 10^{-11}$ cm/W for Fused Silica SQ (Quartzschmiele Ilmenau, Germany), obtained in Ref. 7. It should be noticed that the data from Ref. 7 were normalized on the experimental laser pulse duration and/or the beam cross section, measured in the present work. Our β values for fused silica agree well with the results of Ref. 13; however, they are 2.5–3 times lower than the data, reported in Ref. 14.

The linear approximation used in the case of pure fused silica also allows for the determination of the T_0 value and hence the α coefficient at $\lambda = 264$ nm for the above-mentioned glasses. In calculations we used the refractive indices of Suprasil, Herasil, and Infrasil at this wavelength, $n = 1.5007$, 1.5022, and 1.5022, respectively,[15] the reflectivity of the sample at normal incidence was determined according

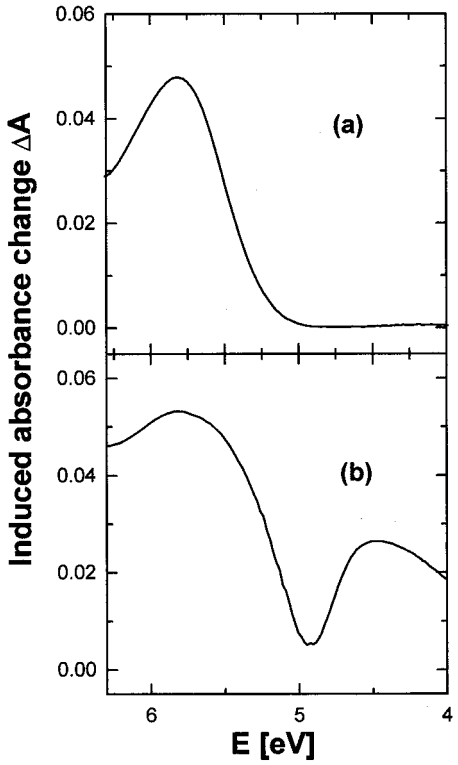

FIG. 2. The difference absorption spectra for (a) 0.1 cm thick Infrasil sample and (b) 0.085 cm thick Ge-doped sample after the femtosecond 264 nm irradiation with intensities 19 and 14 GW/cm^2 and incident fluences 45.9 and 1.6 J/cm^2, respectively.

to Fresnel formula, $R=(n-1)^2/(n+1)^2$. The averaged linear absorption coefficient values are $0.006\pm0.006\ \mathrm{cm}^{-1}$, $0.040\pm0.004\ \mathrm{cm}^{-1}$, and $0.042\pm0.004\ \mathrm{cm}^{-1}$ for Suprasil, Herasil, and Infrasil, respectively, which agree reasonably well with direct spectrophotometric data (see above).

Figure 1(d) shows a typical transmittance-irradiance graph for 3.5 mol % germanosilicate glass and the fitting curve. In this fitting procedure we used the general expression Eq. (3) with experimental values R and α used as parameters. In order to extract the TPA coefficient β from the measured curves, a program was written (software package MATHEMATICA, Wolfram Research Inc.), which calculates β_i for each i value of the measured transmittance curve. The overall β value was determined as the arithmetic average of all the β_i related to one curve. In the calculations, we used for the reflectivity value R of germanosilicate glass at 264 nm, the corresponding value for fused silica. This assumption is based on the fact that the refractive indices for pure fused silica and for the one with 3.5 mol % GeO_2 in the visible range are very similar.[16] Concerning the linear absorption coefficient, the situation with germanosilicate glass is more complicated than in the case of undoped fused silica. In a separate experiment we have irradiated the Ge-doped and Infrasil fused silica samples and found that the femtosecond UV irradiation changed the 264 nm absorption of the Ge-doped silica noticeably in comparison with Infrasil (Fig. 2). The spectrum of induced absorption in the germanosilicate glass after 1 min exposure time [Fig. 2(b)] demonstrates an absorbance change of about 0.02 at 264 nm, which equals a change in α of $0.54\ \mathrm{cm}^{-1}$. Therefore, when fitting the transmittance curves for the germanosilicate glass, we used the mean α value for nonirradiated and irradiated germanosilicate glasses $[\alpha=(2.8+0.54\ \mathrm{cm}^{-1})/2=3.07\ \mathrm{cm}^{-1}]$. For our Ge-doped fused silica sample, four curves were recorded. In Table I the overall TPA coefficients for each recorded curve are presented together with the average for all series of measurements, $(42\pm3)\times10^{-11}$ cm/W, which is 21–26 times higher than β values for pure fused silica.

From Fig. 2 it can also be seen that the induced absorbance changes at 5.8 eV at the similar irradiation intensities for Infrasil and Ge-doped fused silicas are the same for input fluences differing 24 times (taking into account the difference in sample thickness). This corresponds to the difference in the TPA coefficient for these two samples (21 times) and disagrees with the difference in the linear absorption coefficient (154 times). This is a strong argument in favor of the TPA mechanism of the induced absorption change.

In conclusion, we have shown that the doping of fused silica by 3.5% mol Ge leads to the increase of the TPA coefficient at 264 nm by 21–26 times due to the lowering of the band-gap energy.

The authors would like to thank Dr. Andy Ruth and Dr. Miloslav Pravda for their support.

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